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OF DIATOMIC MOLECULES  
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CALCULATIONS OF THE INTERACTIONS  
OF DIATOMIC MOLECULES WITH SOLID SURFACES<sup>†</sup>

by

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CALCULATIONS OF THE INTERACTIONS  
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Abstract

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Three dimensional classical interactions of homonuclear diatomic gas molecules with fcc solid surfaces are calculated by digital computer. The results are compared to matched monatomic interactions previously reported, and to a phenomenological model which gives algebraic expressions for the energy exchanges. Diatomic results indicate an important reduction in energy and tangential momentum transmitted to the lattice, but a slight increase in gas exit energy over the monatomic cases. Diatomic particles experience significantly less lateral scattering than do monatomic. Vibrational energy changes are small except at high energy, and rotational energy change varies linearly with incident translational energy.

Symbols

*Author*

A	correction for attractive potential
d	unit of length ( $= \frac{1}{2}$ lattice spacing)
E	energy
F	force
G	steric factor in vibrational accommodation
IOL	independent oscillator lattice
k	Boltzmann's constant
$k_e$	effective spring constant
m	mass

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$n$  number of lattice atoms/ $d^3$ ; also number of degrees of freedom of gas particle  
 $p$  momentum  
 $P$  probability of subscripted event  
 $T$  temperature  
 $V$  velocity  
 $\alpha$  energy exchange ratio (primes denote various stages of interaction analysis)  
 $\Gamma$  orientation of rotational velocity at impact  
 $\epsilon$  depth of Lennard-Jones 6-12 gas-surface potential  
 $\eta$  fraction of incident flow that is trapped  
 $\theta$  angle between velocity vector and normal to surface  
 $\mu$  mass ratio (lattice/gas)  
 $\mu'$  effective mass ratio for vibrational accommodation  
 $\xi$  shape factor  
 $\sigma$  range parameter of Lennard-Jones 6-12 potential  
 $\sigma_L$  lateral momentum accommodation coefficient  
 $\sigma_t$  tangential momentum accommodation coefficient  
 $\sigma_v$  intramolecular spacing  
 $\sigma_z$  normal momentum accommodation coefficient (the normalized vectorial normal momentum difference between incident and reflected molecule)  
 $\tau$  time interval  
 $\psi$  orientation angle at impact  
 $\omega$  frequency (rad/sec)  
 $\Omega$  dimensionless frequency parameter ( $= \omega_n d / V_i$ )  
 $\bar{F}$  mean of  $F$   
 $s(F)$  standard deviation of  $F$

#### Subscripts

$c$  collision  
 $diss$  dissociation  
 $f$  final state after interaction  
 $g$  gas  
 $i$  initial state  
 $l$  lattice (or solid)  
 $n$  natural frequency of lattice  
 $o$  peak or reference value  
 $r$  rotation  
 $v$  vibration  
 $w$  wall (temperature)  
 $\eta$  related to trapping

## Introduction

An understanding of the important factors in gas-surface interactions at epithermal energy is beginning to emerge from the recent work of many authors (cf. Hurlbut, Ref. 1), but there has been very little information on interactions involving polyatomic molecules. Previous theoretical papers on the effects of internal modes include those of Herman and Rubin (Ref. 2), Feuer (Ref. 3), Allen and Feuer (Ref. 4), and Marsh (Ref. 5), all of which are best suited to those cases in which translational energy is small relative to adsorption energy. It has not yet proven possible to perform quantum calculations with three dimensional geometry, so information on momentum exchange cannot be achieved with these methods.

We know of no data for polyatomic molecules on controlled surfaces at sufficiently high incident energy, that could be used to verify the present results. In connection with the many efforts to achieve such experiments (Ref. 6), the technique of Marsden (Ref. 7) shows promise for characterizing rotational states.

We have previously worked out a theoretical approach to gas-surface interactions of energies above about 0.2 eV which is based on the use of a large digital computer to calculate families of molecular trajectories in the neighborhood of surfaces (Refs. 8-10). The results of these "computer experiments" on monoenergetic parallel beams are then used in the selection of phenomenological models which can be treated by simple mathematics and which show behavior similar to that of the computed trajectories (Ref. 10). There do not appear to be any inconsistencies with the theories based on lattice dynamics (e.g., Goodman, Ref. 11, or Trilling, Ref. 12). Experimental verification is thus far available only from the cell method of measuring thermal accommodation coefficients (data from this source are given by Goodman and Wachman, Ref. 13), but several of the conditions for validity of our theory are violated in these low energy cases.

The present paper has been worked out with the objectives of identifying the major factors in the partitioning of energy among the various degrees of freedom in diatomic interactions, and of finding the main differences in the translational energy and momenta between diatomic and related monatomic interactions. We have chosen the homonuclear diatomic case for its simplicity and wide importance.

## Diatomic Trajectory Calculations

The calculations of classical trajectories for model diatomic molecules were carried out along lines similar to those used for the monatomic cases (Refs. 8-10). Twelve first-order differential equations describe the motion of the two atoms in three dimensional Cartesian coordinates. The polar orientation and velocity components are found by trigonometric transformations at any desired time. A mutual restoring potential of the Lennard-Jones 6-12 type is used. We have restricted our development to homonuclear molecules, and have employed the law of conservation of energy as a check on the accuracy of the computation. Rotational-vibrational coupling is inherent in the model.

We use classical mechanics in the calculations. Rapp (Ref. 14) and Treanor (Ref. 15) have shown that the classical model gives good results for vibrational energy exchange when averaged over impact parameters and orientations in gas-gas collisions. Gilbey and Goodman (Ref. 16) show that the monatomic classical model is adequate if  $E_i$  is high so that transition levels in the lattice are closely spaced relative to  $E_i$ . Photon emission times are many orders of magnitude greater than interaction times, so radiation can be ignored. Rotational levels will be closely spaced relative to  $E_i$ . We feel the classical model is worthwhile because of its ability to handle complicated geometry.

The Lennard-Jones 6-12 potential was selected for all interatomic forces involving the gas particles because it displays the major features of real interactions in a form which is readily related to physically measurable quantities by two parameters, and because it avoids the use of exponentials or other functions, the calculation of which is very time-consuming. We write the intramolecular potential as,

$$\Phi_{\text{int}} = 4 E_{\text{diss}} \left[ \frac{1}{2} (\sigma_v/r)^6 - \frac{1}{4} (\sigma_v/r)^{12} \right] - E_{\text{diss}} \quad (1)$$

where  $r$  is the distance between atomic centers. All molecular properties are assumed to be due to the superposition of equal atomic contributions.

Calculation of the intramolecular motion usually requires a large number of time steps. To minimize this expenditure, we calculate the motion of an equivalent monatomic particle until the incident molecule gets close to

the lattice, when the internal degrees of freedom are "turned on." The criterion employed for this switch is based on the continuum approximation to the long-range forces between the complete crystal and a single gas atom. The internal structure is activated when the single-atom attraction at the molecular center of mass is a few percent different from that for an atom one-half atomic spacing closer to the lattice. A random number generator selects initial phase angles for vibration, rotation, and the orientation of the molecule. The initial rotational and vibrational energies are assigned as independent input quantities, and are constant for all molecules of a given case. After activation the trajectory proceeds with full diatomic mechanics until it has once more left the immediate vicinity of the lattice. If the molecule has not been dissociated, its constituent atoms are again combined into a point mass with equivalent molecular properties and the internal energy distribution at that instant is recorded as output. Concurrent with this patching together of molecular models, we use the matching procedures described in Ref. 8 to portray the potential field felt by the gas atoms. The semi-infinite distribution of long range potential sources is essential to give consistent momentum histories.

The output for a given trajectory gives the exiting translational, rotational and vibrational energies, the three components of exit momentum, the normal and azimuth angles of the exit translational velocity, the total energy transmitted to the lattice, an indication of dissociation and/or trapping, and the net change (i.e., error) of energy in the calculation. Trajectories were run in groups of 8 (a  $5 \times 5$  grid on the surface of a unit cell, reduced by symmetry), except for two cases which were run with 18 (a  $7 \times 7$  grid). The output parameters described above were averaged and their standard deviations calculated. Forty-eight useful cases have been run in all, of which the first 16 are exploratory, the second 16 correspond to equivalent monatomic cases taken from the first 16 runs of the planned design of Ref. 9, and the last 16 represent a model  $N_2$  molecule impinging on (110) and (100) Au at different energies and incidence angles. The results and their corresponding input levels are not given here, but are tabulated in Ref. 17. An independent-oscillator lattice model was used throughout this work, as the monatomic work we have done has shown that it should be satisfactory (Refs. 9, 10, 17).

One of the fundamental problems of computer experiments is the great difficulty of assimilating the results. Myriads of numbers are available, each describing some property of a unique interaction. The value of the work rests primarily on the degree to which these results can be formed into a recognizable structure. We have employed three basic approaches: systematic comparison with corresponding monatomic cases, analysis of models to give correlation equations, and treatment of a system of two specific species.

Results were consistent with our earlier monatomic results. One or two lattice atoms still receive practically all of the energy transmitted to the lattice. Atoms are still "trapped" on the surface by lack of sufficient normal momentum, even though they retain a balance of kinetic over potential energy. Very limited testing has indicated that the outermost layer of atoms dominates diatomic interactions in the same way as it does monatomic ones. Vibrational energy exchange is negligible until  $E_i$  exceeds the dissociation energy, but rotational energy exchange appears to be nearly a fixed fraction of  $E_i$  for a given geometry and set of species. Dissociation occurs only when an appreciable fraction of the population receives an amount of energy in the internal modes which exceeds the dissociation energy. It has little or no effect on energy transmitted to the lattice unless the incident molecule is trapped.

The 16 cases that are matched to corresponding monatomic cases from Ref. 9 have been processed to determine the factors that make diatomic interactions behave differently from monatomic ones. Table 1 shows the results of this processing. The number of cases is limited, so we have merely designated the direction of the most important effects (i.e., slopes) from a variance analysis. The tabulated averages show the direction and amount by which diatomic differs from monatomic. Curvatures are indicated by asterisks for those cases in which they indicate an important opposing effect to that of the slope. The presence or absence of a particular sign may ultimately prove to be an artifact of the design, the method of analysis, or of coincidence, but we feel that a generous majority of the indications are reliable.

Hayward and Trapnell (Ref. 18) indicate that  $N_2/Au$  is unlikely to form chemical bonds. The N-Au bond was assumed to be 0.05 eV with a L-J  $\sigma$  of 2 Å. The old value of 7.35 eV was used for the N-N bond, with 1.09 Å for  $\sigma_v$



(Ref. 19). The actual  $E_{\text{diss}}$  of 9.76 eV would not change the results, except to further reduce the observed small vibrational accommodation. Kittel (Ref. 20) gives 4.07 Å as the lattice spacing ( $d = 2.04$  Å) and 165°K as the Debye temperature. Figures 1-3 give the results for the fcc (100) face of Au. The points shown as predicted values are discussed in the next section.

Comparison of data from (100) and (110) fcc surfaces showed significant increases in scattering for the (110) case, as measured by larger standard deviation values. Rotational energy changes, tangential momentum accommodation, and exit angle measured from the normal were greater for the (110) case, while exit normal momentum was less. Energy transmitted to the lattice was significantly greater for the (110) case for high  $E_i$ , but no significant difference was found at lower energies where attraction is the dominant mechanism. The lateral scattering momentum showed an opposite dependence on energy, being about the same at high energy, but being markedly greater for (110) for the low energy cases. All of these runs were made at an azimuth angle of 22.5° from the line of closest packing on each surface.

#### Phenomenological Model for Energy Exchange

In Ref. 10, an analysis of energy exchange in monatomic interactions was carried out by considering the lattice as a single harmonic oscillator. The gas particle's effect was represented by a force pulse with a shape selected by trial of several forms, an amplitude which was derived from the momentum exchange in an equivalent hard sphere collision, and a temporal duration determined by correlation of about 1500 computed trajectories. The equations of motion were then integrated over the duration of the force pulse and solved for the energy transmitted to the lattice. Analytical corrections were introduced for off-normal angle of incidence, long-range attractive forces of the lattice, trapping after primary collisions, surface contaminants, and initial thermal motion in the lattice. The results of the monatomic analysis, when used to "predict" the energy exchange of the computer experiments, showed no systematic discrepancies and gave a scatter which has a standard (i.e., rms) error of about 10 percent of the incident energy. The analysis therefore gives a simple correlation of many of the results of Ref. 10 that is for practical purposes as reliable as the trajectories themselves. It also gives a physical picture of the mechanisms involved and their relative

importance in a given situation. We now extend the monatomic analysis to the diatomic case.

The over-all interaction is considered in several parts; an equivalent monatomic interaction, a rotational and vibrational excitation, and an exiting from the lattice. The separate parts are then superposed and several adjustable parameters are iterated to find the values which conform best to the computed trajectories.

At least three extreme modes can be visualized for a diatomic impact: 1) the atoms can act jointly as a single mass which can absorb internal energy; 2) they can act as two independent particles; or 3) one atom can rebound, and carry the second atom away from significant interaction with the lattice. In the 48 cases calculated for this report the first case is the most prevalent, but when the gas molecule is much lighter than the lattice atoms, or the angle of incidence decreases toward the surface parallel, we find the second case yields a better prediction. From the well-known hard sphere law (HSL) for interaction along lines of centers, the energy left in the target atom is  $4\mu E_i / (1 + \mu)^2$ . Two independent masses, each of  $m_g/2$ , would leave a total of  $8\mu E_i / (1 + 2\mu)^2$  in the lattice. This behavior is found in the trajectories when  $\mu \gg 1$ , or when  $\theta_i \rightarrow 90^\circ$ . We have therefore represented the HSL as a composite form which obeys the required limits:

$$\alpha_{\text{HSL}} = \frac{4\mu - 2(\mu - 1)\sin \theta_i}{(1 + \mu)^2} \quad (2)$$

Equation (2) is not intended at this stage to represent anything except a head-on, normal impact. In Ref. 10 we found that off-normal incidence was correlated by a factor of  $-\cos \theta_i$  on the RHS of Eq. (2), and this has been confirmed by Goodman (Ref. 11) who also introduced an empirical correlation factor to account for non-head-on effects. Goodman's value of 0.90 for this factor agrees with 0.894 produced by an iteration on the results of our Ref. 10.

The next factor is correction for the dynamic effects of lattice restraining forces. Reference 10 gives an expression for the energy exchange for a simple harmonic oscillator driven by a force pulse of the assumed exponential

form  $F = F_0 e^{-\frac{1}{2}(t/\tau_c)^2}$ ;

$$\alpha' = \frac{2\pi(F_0\tau_c)^2}{\mu} e^{-(\omega_n\tau_c)^2} \quad (3)$$

When  $F_0$  and  $\tau_c$  are determined by employing the modified HSL of Eq. (2) to determine the impulse felt by the lattice oscillator, and the above corrections are added, we are left with

$$\alpha'' = -0.9 \cos \theta_i \alpha_{\text{HSL}} e^{-(\omega_n\tau_c)^2} \quad (4)$$

The characteristic time of collision for a large group of monatomic interactions was found in Ref. 10 to be  $(\tau_c)_{\text{Mon}} \simeq 0.105 \sigma/V_i$ . The diatomic case correlates best with the expression:

$$(\tau_c)_{\text{Diat}} = 0.105 \frac{\sigma + \sigma_v/\sin \theta_i}{V_i} \quad (5)$$

where  $\sigma_v/\sin \theta_i$  is constrained to be  $< \sigma$ . The additional term accounts for an effective broadening of the force pulse when both gas atoms strike a single lattice atom at slightly different times.

The attractive portion of the gas-surface potential is very important at low  $E_i$ . We correct here only for its intensification of the impact by a simple factor of  $(1 + A)$  on the RHS of Eq. (5). Its effect on trapping will be studied later. The parameter  $A$  is a normalized bonding energy, obtained for Ref. 10 by integration over a semi-infinite lattice, and here modified for the uncontaminated diatomic case to be

$$A_{\text{Diat}} = \frac{2\pi n}{3E_i \cos^2 \theta_i} \epsilon \left( \frac{g}{d} \right)^3 \frac{1 + \xi_\eta^3}{(1 - \xi_\eta^2)^3}, \quad \xi_\eta = 0.69 \frac{\sigma_v}{\sigma}, \quad (6)$$

where 0.69 is determined empirically. The last factor of Eq. (6) accounts for the fact that the closer atom shows a stronger effect in a cubic potential field than if it were at the molecular center of mass. The empirical factor gives the mean effect of this orientation in the assumed model for our 48 cases.

The forces which cause changes in the vibrational energy of the molecule are very similar to those which drive the lattice oscillator. We get the best results with the assumption that the second gas atom in effect rebounds from its mate while the latter is in contact with the lattice atom. Using the analog of Eq. (3), we find

$$\frac{\overline{\Delta E_v}}{E_i} = G \frac{2\mu'}{(1 + \mu')^2} \left( 2 - e^{-k_\ell/k_v} \right) e^{-(\omega_v \tau_v)^2}, \quad (7)$$

where  $G$  is a steric factor of 0.32 from our 48 cases,

$$\mu' = \frac{m_g/2}{m_g/2 + m_\ell}, \quad \tau_v = 0.105 \frac{\sigma_v + \sigma_v/\sin \theta_i}{v_i},$$

$$\omega_r = \frac{12.0 v_i}{\sigma_v} \sqrt{\frac{E_{diss}}{E_i}}, \quad \text{and} \quad k_\ell/k_v = 4\mu \left( \frac{\omega_r}{\omega_v} \right)^2$$

The full translational energy ( $E_i$ ) is coupled to the internal oscillator through the modified HSL only when the lattice springs are very much stronger than the intramolecular spring. In the opposite limit of very weak lattice springs, only half of that amount is available because the recoil energy given to the lattice by the first atom to strike can never be returned to the molecule's internal motion.

Rotational energy accommodation depends primarily on the geometry of the encounter. We estimate the relative motion induced by one atom moving tangential to the surface while the other of the pair is stopped at the surface. The effective rotational velocity depends on random orientation at impact and on molecular shape because the contact atom may be "kicked back" so as to oppose the rolling mode. We write

$$\frac{V_r}{V_i} = \frac{\sin \theta_i}{2} \sin \psi + \xi_r \cos \theta_i \cos \psi + \sqrt{\frac{E_{ri}}{E_i}} \sin \Gamma \cos \psi, \quad (8)$$

where  $V_r$  is measured relative to the molecular center of mass, and the phase angles  $\Gamma$  and  $\psi$  will independently vary uniformly from 0 to  $2\pi$ . The parameter  $\xi_r$  is a rotational shape factor which is defined as

$$\xi_r = \frac{1.38 \sigma_v/\sigma}{1 + 1.38 \sigma_v/\sigma}, \quad (9)$$

where 1.38 is again empirically determined.

The mean exit rotational energy can be expressed as an integral of  $(v_r/v_i)^2$  over all values of  $\Gamma$  and  $\psi$ , and becomes

$$\overline{\Delta E_r}/E_i = \frac{1}{8} \sin^2 \theta_i + \xi_r^2 \cos^2 \theta_i - \frac{3}{4} \frac{E_{ri}}{E_i}. \quad (10)$$

The first term represents a rolling effect on the surface, the second a "kickback" effect which only occurs near normal incidence for elongated molecules, and the last term the effect of initial rotation.

The distribution of internal states should be uniform over the interval from 0 to  $2 \overline{\Delta E_r}/E_i$ . Since  $\Delta E_v/E_i$  appears to depend on the cosine of the angle between the incident path and the molecular line of centers, we would expect  $E_v$  to be nearly uniformly distributed from 0 to  $2 \overline{\Delta E_v}/E_i$ . We therefore assume uniform distribution of internal energy, and use this distribution to calculate the predicted probability of dissociation:

$$P_{diss} = 1 - \left\langle \frac{E_{diss}}{2(\overline{\Delta E_v} + \overline{\Delta E_r})} \right\rangle \quad (11)$$

where the bracketed term is set equal to unity if it should exceed that value.

When a particle dissociates, it loses its rotational energy and gains an equal amount of vibrational energy. This is displayed in the individual trajectories, and has been incorporated into the model as shown below:

$$(\overline{\Delta E_v}/E_i)_f = \overline{\Delta E_v}/E_i + [\overline{\Delta E_r}/E_i + E_{ri}/E_i] P_{diss} \quad (12)$$

$$(\overline{\Delta E_r}/E_i)_f = \overline{\Delta E_r}/E_i - [\overline{\Delta E_r}/E_i + E_{ri}/E_i] P_{diss} \quad (13)$$

Note that this shift of energy in no way affects the total internal energy.

A further effect of attraction is in the trapping of particles having low normal momentum after a primary collision. We assume that the probability of being trapped is an exponential of the ratio of the energy equivalent of the mean exit normal momentum to the effective binding energy:

$$\eta = \exp - \left[ \frac{(1 - e^{-1/A})(1 + A)(1 - \alpha'') - \alpha_{int}}{2qA \cos^2 \theta_i} \right], \quad (14)$$

where  $\alpha_{int} = \overline{\Delta E_r}/E_i + \overline{\Delta E_v}/E_i$  and  $\alpha''$  is given by Eq. (4). The factor of 2 in the denominator of the exponent represents the monatomic empirical factor. The factor  $q$  represents a diatomic correction, and has been found to be

$$q = 0.62 \frac{1 + P_{diss}}{\cos^2 \theta_i} \quad (15)$$

Note that this model indicates that the monatomic dependence on angle of incidence in Eq. (14) is canceled by that in Eq. (15). There is also an increased tendency to trap when probability of dissociation is high.

The model of Ref. 10 shows two separate thermal effects for monatomic interactions; a change in the energy to which trapped particles accommodate, and an increase in the exit energies of untrapped particles whereby thermal motion is felt more strongly with increasing  $\omega_n \tau_c$ . The latter mechanism is absent in our diatomic results. The effect of wall temperature can now be expressed as:

$$E_\ell/E_i(T_w) = E_\ell/E_i(0) - \eta \frac{n+1}{2} kT_w/E_i, \quad (16)$$

where  $n = 7$  for a diatomic molecule. The input data are expressed in terms of  $E_w = 3kT_w$ , the total thermal energy per lattice atom.

We have found from the 48 sets of trajectories that the best results are achieved by subtracting the internal energy increase from the energy transmitted to the lattice (i.e.,  $\alpha''$ ) predicted by Eq. (4). The physical justification for this is that the internal softness lessens the impact on the lattice directly, but its effect on other modes of motion is secondary. The final expression for the average energy transmitted to the lattice becomes

$$\begin{aligned} \overline{E}_\ell/E_i = & \alpha''(1 - \eta)(1 - \alpha_{\text{int}}) + \\ & + \eta\left(1 - \frac{n+1}{2} kT_w/E_i\right)\left(1 + \frac{E_{ri}}{E_i} + \frac{E_{vi}}{E_i} - P_{\text{diss}} \frac{E_{\text{diss}}}{E_i}\right). \end{aligned} \quad (17)$$

The last term in Eq. (17) describes for the trapped molecules the energy left in the lattice by internal modes and in the form of dissociation energy released.

The exit translational energy can now be found by conservation of energy:

$$E_g/E_i = 1 - \overline{E}_\ell/E_i - \alpha_{\text{int}}. \quad (18)$$

The predictions of the above model have been compared against the results of the 48 sets of 8 trajectories. Each of the empirical parameters has been determined by using the mean error in the variable it influences to correct its value for the next iteration. The results for  $\overline{E}_\ell/E_i$  are plotted in Fig. 4 for comparison. The predictions are shown for the  $\text{N}_2/\text{Au}$  (100) cases in Figs. 1-3. All of the results and predictions are tabulated in Ref. 17.

The over-all prediction quality for internal energy change can be assessed from the standard (rms) error of  $0.060 E_i$  and mean-magnitude error of  $0.047 E_i$ , compared to a mean internal energy change of  $0.115 E_i$  in the 48 cases. The corresponding values for  $E_\ell$  are 0.095, 0.073, and  $0.342 E_i$ .

#### Over-all Results and Conclusions

The results and conclusions have two important qualifications. First, they represent a classical approximation to the real mechanics of the interaction. Second, the number of trajectories for a given input condition is severely limited by computing time, and the average values for individual cases can show scatter from "infinite sample" values. Also, coupling confuses the separation of vibrational and rotational energy for weakly bound molecules. Taken as a group, however, we feel that the present results represent reliable trends for classical calculations of realistic interactions.

Vibrational excitation during impact occurs to a significant degree only when  $E_i \gg E_{\text{diss}}$ . Dissociation be-

comes probable in proportion to  $(\overline{E_{int_f}} - E_{diss})$ . Rotational energy exchange appears to be controlled primarily by geometric considerations.  $\overline{\Delta E_r}/E_i$  is nearly constant with  $E_i$ , usually decreasing as the incident ray becomes more normal. Energy absorbed by the internal degrees of freedom noticeably reduces the energy transmitted to the lattice when compared to a matched monatomic case. A slightly increased exit translational energy is probably due to the fact that a diatomic molecule acts like a larger, lighter monatomic gas atom. Diatomic particles are reflected with more directivity than are equivalent monatomic particles. The average tangential momentum accommodation for 16 cases is about half that of monatomic particles, while the mean exit normal momentum is slightly greater. Most of this added directivity comes from a reduction in lateral scattering from that of the monatomic equivalents. Energy exchanges in the classical model represented by the computed trajectories can be satisfactorily represented by a model composed of the superposition of several types of mechanical interactions. Several important differences in interactions can be attributed to differences in crystal orientations. Higher values for the standard deviations of all translational interaction parameters were shown for the (110) case over the (100) case of  $N_2/Au$ . The (110) surface being quite directional and atomically rough, this increased scattering should be expected.

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TABLE I  
Comparison Table for 16 Matched and Balanced Pairs  
of Computed Diatomic and Monatomic Cases

Output Parameter	Average Diatomic Value	Average Difference (D-M)	Variables which have Important Effects on Differences (+ indicates D-M Increases with Increase in Variable)								
			$\Omega^2$	$a/d$	$\epsilon/E_i$	$E_{diss}/E_i$	$E_w/E_i$	$E_{vi}/E_i$	$E_{xi}/E_i$	$\sigma_v/d$	$\theta_i$
$\overline{\eta}$	0.136	0.018	+	-	+				-	+	-
$\overline{E_g}/E_i$	0.640	0.096	-		+			+	+		+
$\overline{E_l}/E_i$	0.342	-0.232	+		-	+	+			+	-
$\overline{\sigma_z}$	1.832	0.038		-		-	-				+
$\overline{\sigma_t}$	0.305	-0.315	-	-	-			-	-	+	-
$\overline{\cos \theta_f}$	0.617	-0.026		-	-	+	-	-	+		+
$s(E_g/E_i)$	0.142	0.029	+	+							
$s(\sigma_z)$	0.197	-0.118		+	-		-		+	-	+
$s(\sigma_t)$	0.187	-0.097		+			+		-	+	
$s(\sigma_c)$	0.482	-0.152	-	+		+			-		-
$s(\cos \theta_f)$	0.140	-0.067		+			-				
$s(\phi_f)$	52.7°	-16.15°	-	-	-	+	-		-	+	
$\Delta E_v/E_i$	0.063		-*			-	-	-*	-	+	-
$\Delta E_r/E_i$	0.039		+	-	+		-	+	+	+	
$P_{diss}$	0.191		-*			-	-				-
$s(E_{vf}/E_i)$	0.071			+			-	-	-	+	
$s(E_{rf}/E_i)$	0.062			-		+	+	-	+	+	

\* Curvature (i.e.,  $\frac{\partial^2 \text{Output}}{\partial \text{Input}^2}$ ) is significant, and of opposite sign.

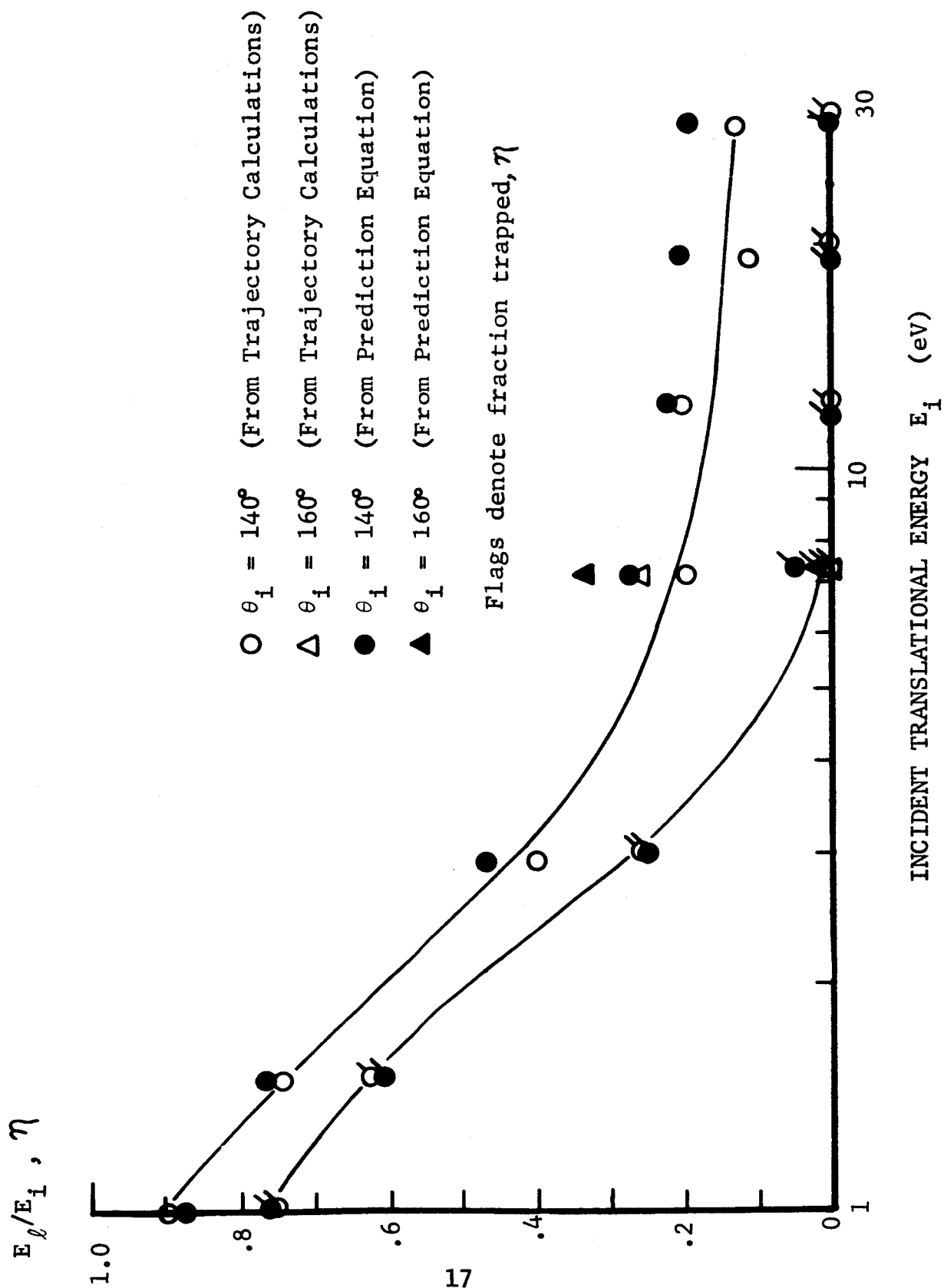


Fig. 1 Energy transmitted to lattice and fraction of incident flux which is trapped -  $N_2/Au(100)$

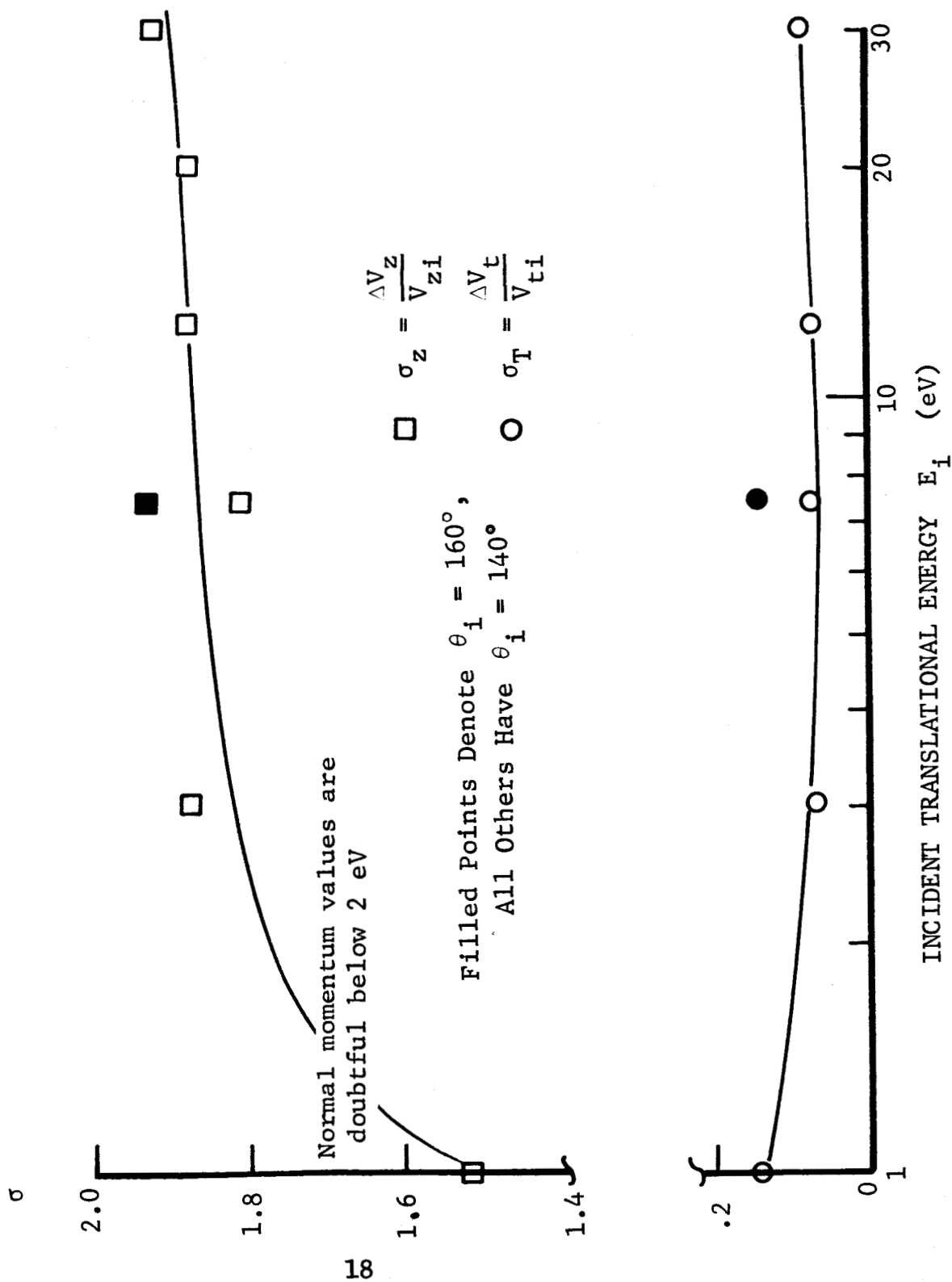


Fig. 2 Momentum exchange coefficients -  $N_2/Au(100)$

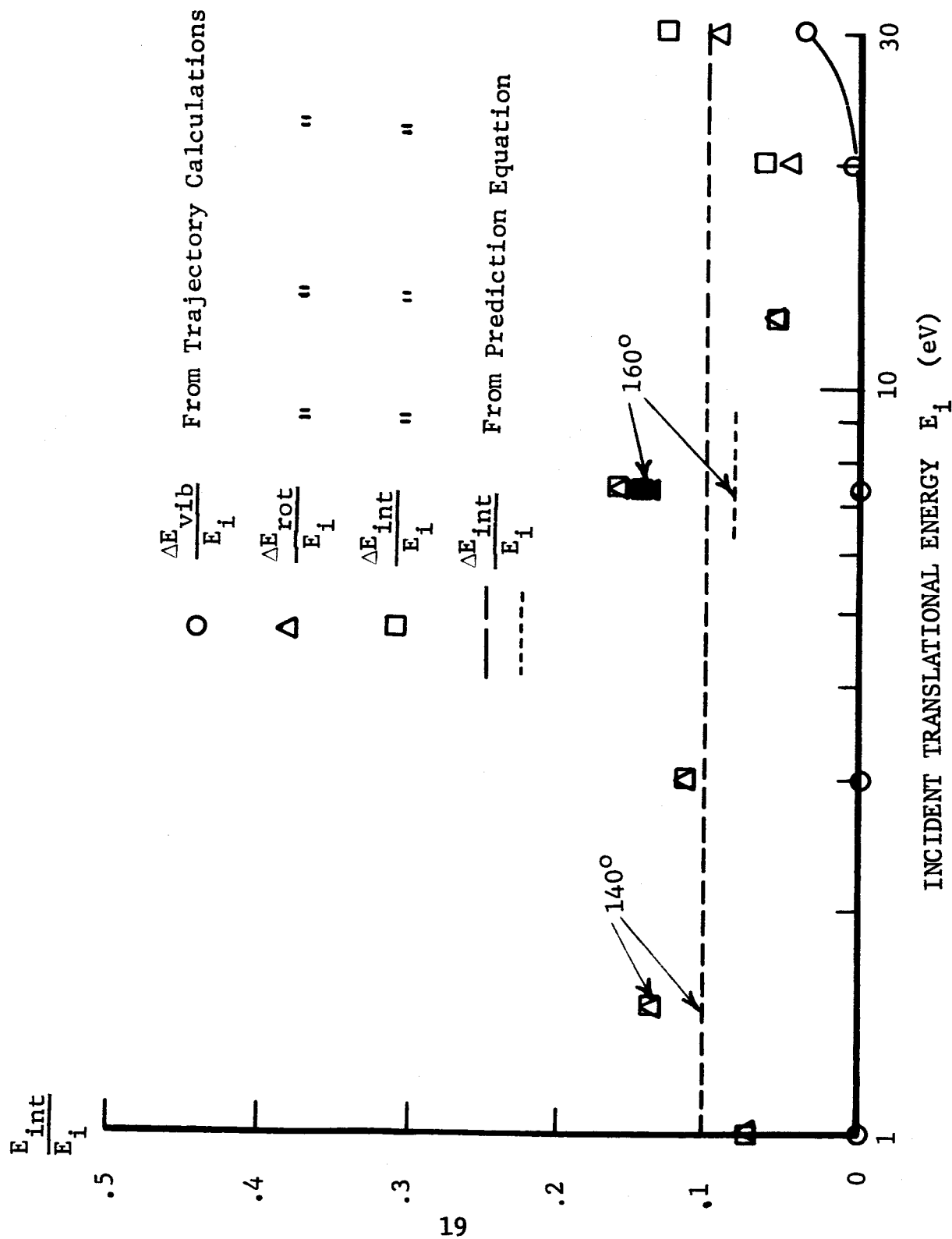


Fig. 3 Changes in internal energy -  $N_2/Au(100)$

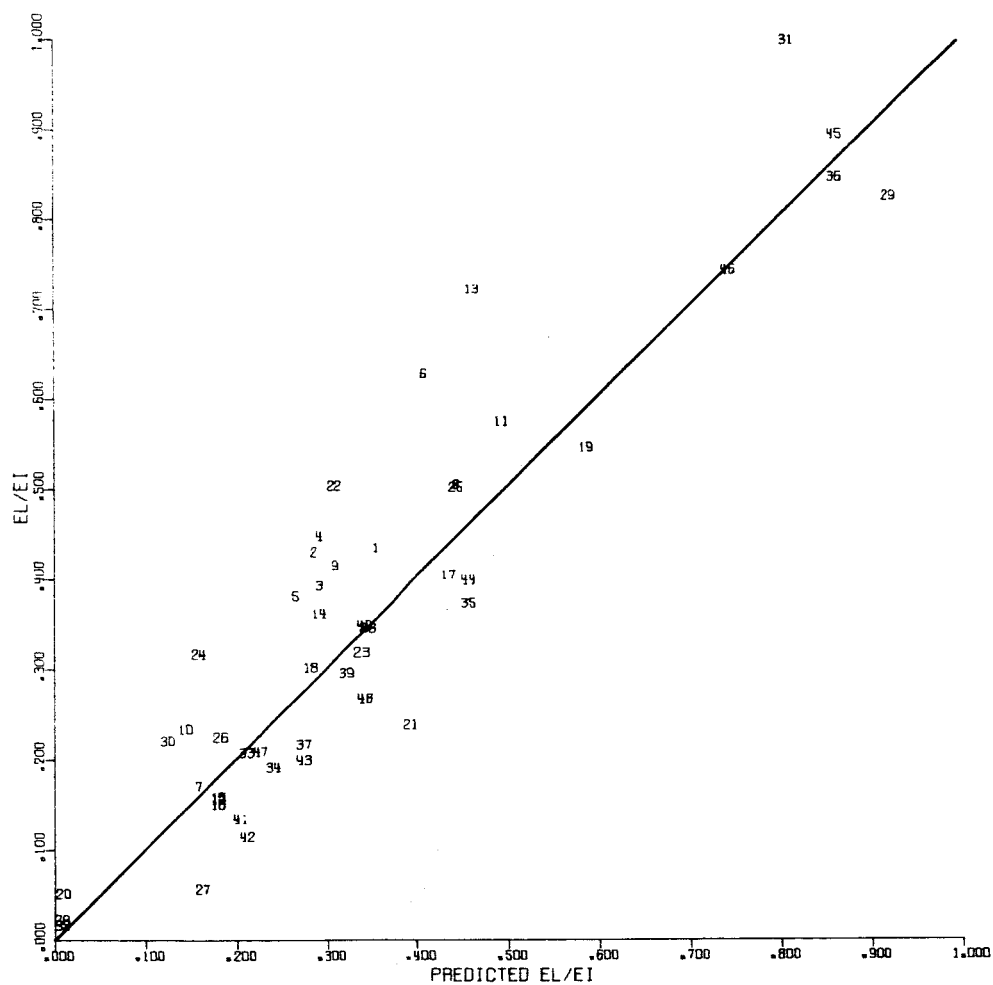


Fig. 4 Fraction of incident translational energy transmitted to lattice in 48 sets of trajectory calculations compared to predicted energy exchange for diatomic molecules

CALCULATIONS OF THE INTERACTIONS  
OF DIATOMIC MOLECULES WITH SOLID SURFACES

by

R. A. Oman

Fluid Mechanics Section

ERRATA

Page 4     Eq. (1) should read:

$$- \Phi_{\text{int}} = \dots\dots\dots$$

Page 9     Second Paragraph, 4th line:

... on the RHS of Eq. (5).....

should be changed to read:

... on the RHS of Eq. (4). ...

Page 11    Third Paragraph, 1st line:

Change the word "internal" to "rotational"

Page 13    First part of Eq. (17) should read:

$$\bar{E}_l/E_i = \alpha'' (1 - \eta) (1 - \alpha_{\text{int}}) (1 + A) + \dots$$